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9. SPONSORING/MONITORING AGENCY REPORT NUMBER AFOSR-86-0054	10. SUPPLEMENTARY NOTES  <b>DTIC SELECTED SEP 14 1992</b>	11. ABSTRACT (Maximum 200 words)  A time-resolved ir absorption spectrometer capable of detecting chemical transients on the nanosecond timescale was designed, constructed, and successfully implemented. The spectrometer was used to characterize the vibrational relaxation of an open shell radical species, CF <sub>3</sub> , produced with excess energy from the photolysis of the parent CF <sub>3</sub> I compound. The effects of vibrational excitation in the CF <sub>3</sub> radical on the reaction CF <sub>3</sub> + Br <sub>2</sub> → CF <sub>3</sub> Br + Br were measured. Broadband data collection techniques were used to monitor the reactive and relaxation pathways simultaneously. The energetic radicals react no faster than the thermalized CF <sub>3</sub> and may actually have a lower cross section for reaction. The spectrometer was also used to detect the gas phase absorption spectra of the polyatomic radicals.  A thorough investigation into ozone-olefin reactions in a cryogenic matrix environment was completed. It was possible to complex ozone with various olefinic partners through careful control of the matrix deposition process, despite the very low (1-5 kcal/mole) activation energies for the ozonolysis reactions. The ground state complexes were observed to form a charge-transfer (CT) complex upon excitation.	12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; Distribution unlimited.		
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## **FINAL REPORT**

**ELECTRONICALLY EXCITED MOLECULES: REACTION KINETICS  
AND EMISSION OF LIGHT: NANOSECOND INFRARED SPECTROSCO-  
PY, ELECTRONIC EMISSION FROM CHEMICAL REACTIONS**

**AFOSR-86-0054**

**November 1, 1986 - April 15, 1991**

**Principal Investigator: Professor C. Bradley Moore**

**for the late Professor George C. Pimentel**

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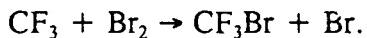
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## PROJECT SUMMARY

The support provided by the Air Force Office of Scientific Research, under grant number AFOSR-86-0054, made significant progress possible in several areas related to elucidation of energy paths of chemical reactions. A time-resolved ir absorption spectrometer capable of detecting chemical transients on the nanosecond timescale was designed, constructed, and successfully implemented. The spectrometer utilizes a home-built dye laser to convert visible radiation to broadband ir radiation through stimulated electronic Raman scattering in cesium metal vapor. The ir light, centered at  $10 \mu$  serves as the probe for chemical reactions induced by a uv excimer laser. We preserve the broadband nature of the probe by employing a linear ir detector array, composed of 128 mercury-cadmium-telluride elements. This is the first known use of these powerful detectors in a time-resolved spectroscopic experiment. Details of the instrument have been published (Refs. 1 and 2).

The spectrometer was used to characterize the vibrational relaxation of an open shell radical species,  $\text{CF}_3$ , produced with excess energy from the photolysis of the parent  $\text{CF}_3\text{I}$  compound. The results have been published (3) and provide evidence that the excess energy is localized in symmetric modes of the radical, consistent with molecular beam photodissociation studies. The rare gas collision partners, He and Ar, have similar relaxation efficiencies which is indicative of a  $V \rightarrow V, T$  process with modest energy defects. The polyatomic buffer gas,  $\text{CO}_2$ , is 4 times more efficient than the rare gases and reveals the action of a new relaxation pathway: a  $V \rightarrow V'$  process from the  $\text{CF}_3$  umbrella mode at  $701 \text{ cm}^{-1}$  to the  $\text{CO}_2$  bending mode at  $673 \text{ cm}^{-1}$ . These studies have contributed significantly to the hitherto sparse knowledge concerning energy transfer processes involving radical species and were made feasible by the broadband capabilities of our spectrometer.

We have built upon these studies and completed an investigation (4) on the effects of vibrational excitation in the  $\text{CF}_3$  radical on the reaction:



Using our broadband data collection techniques, we were able to monitor the reactive and relaxation pathways simultaneously. We found that the energetic radicals react no faster than the thermalized  $\text{CF}_3$  and may actually have a lower cross section for reaction. Dynamical factors that result in poor coupling of the vibrational energy, residing in symmetric modes, to the reaction coordinate could be responsible for our experimental observations. In addition,

we made an independent determination of the rate for the bromine abstraction reaction which agrees well with low pressure photolysis studies.

We have also utilized the completed spectrometer to detect the gas phase absorption spectra of other polyatomic radicals; C<sub>2</sub>F<sub>5</sub>(2) and C<sub>2</sub>F<sub>3</sub>(5,6). The C<sub>2</sub>F<sub>3</sub> experiments were conducted in conjunction with a high-resolution ir diode laser spectrometer. It appears that the use of our broadband spectrometer to locate ir bands of transient molecules will considerably facilitate their subsequent study with diode lasers, which have superior resolution but are not as easy to use in the search for unknown spectral features. Finally, we began experiments to obtain the ir absorption spectra of photoproduced triplet state species. This is a particularly interesting avenue of study since there is a dearth of information concerning the ir bands of triplet states. We performed initial experiments in the gas phase and in the liquid phase using cryogenic liquid xenon, a solvent with many interesting properties. The gas phase studies have been promising and we are preparing a manuscript on our experiments with perfluoropyridine(7).

In a study in liquid rare gases, we have monitored intermolecular alkane C-H oxidative addition by infrared laser flash kinetic spectroscopy.

We completed a thorough investigation into ozone-olefin reactions in a cryogenic matrix environment (8). We were able to complex ozone with various olefinic partners through careful control of the matrix deposition process, despite the very low (1-5 kcal/mole) activation energies for the ozonolysis reactions. The ground state complexes were observed to form a charge-transfer (CT) complex upon excitation with visible/uv radiation. Our published results (9) show that the wavelength of the CT band correlates with the ionization potential of the olefin donor species as expected. We were also able to discern that the CT states have a dipole moment on the order of 17 D and a lifetime of 1-10 ps. The formation of a strong intermolecular bond in the CT complex is inferred from the spectroscopic observations. In the case of allene-ozone complexes, a chemical reaction was found to proceed readily upon excitation with red light. We detected several products, including the new species allene oxide and propadienol (10,11). A most interesting observation was a change of the product branching as Ar was replaced by Xe as matrix material. This was interpreted by access to an excited triplet reaction surface in Xe but not in Ar, establishing a

case of bimolecular photochemical reaction path control by the external heavy atom effect of the solid matrix environment.

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